

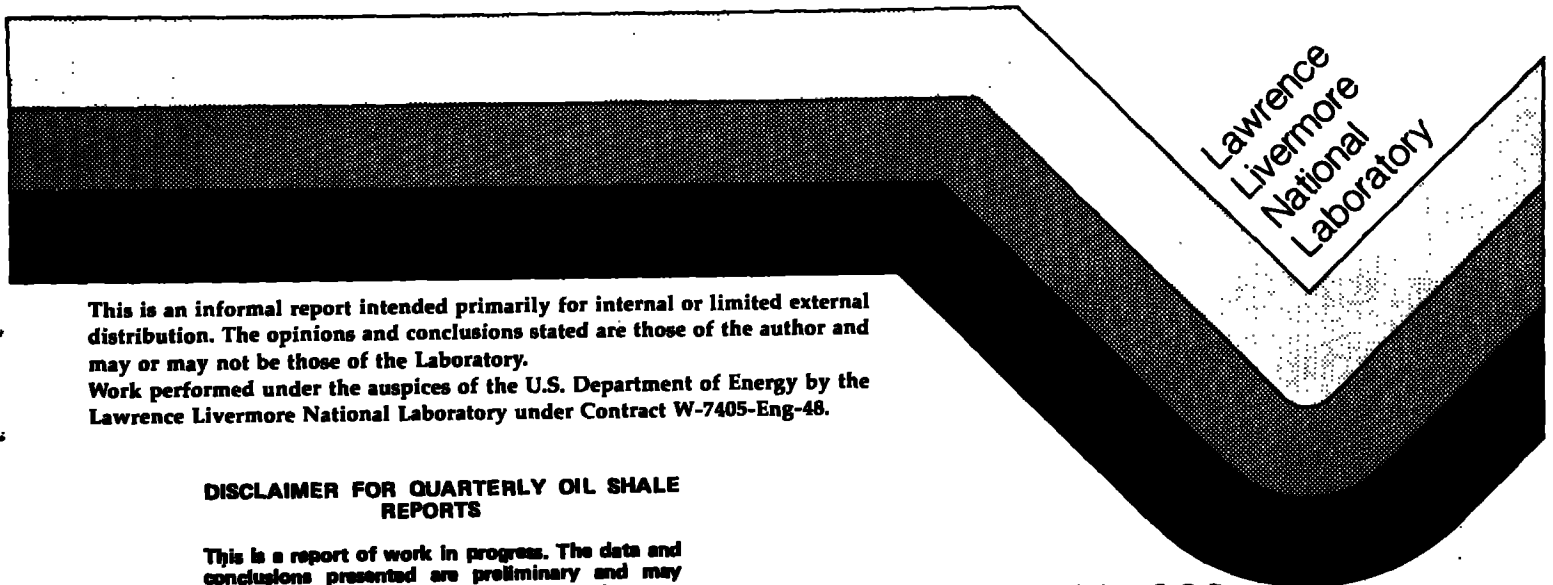
LAWRENCE LIVERMORE NATIONAL LABORATORY
OIL SHALE PROJECT QUARTERLY REPORT

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A. E. LEWIS, Editor

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I. RETORT MODELING

Updated base-case calculations for 50,000 barrel/day plants were made for the two hot-solids processes that we have been modeling: the cascading-bed retorting system (HSCB) and the staged, fluidized-bed retort with lift-pipe combustor (HSFB). Recently-revised computer codes and input parameters were used. The base-case operating conditions for both systems were made as similar as possible: 30 gal/ton raw shale grade, 28.5 wt% dolomite, 8.4 wt% calcite, 1.5 wt% bound water, 6.7 mm maximum raw shale particle size, 3.3 : 1 mass recycle ratio, and 3.2 minutes pyrolysis residence time at a mean pyrolysis temperature of 511°C (HSCB) or 513°(HSFB). The raw shale was preheated to 100°C.

Each processes gave an oil yield of nearly 99 percent of Fischer assay (based on a maximum possible oil yield of 105% F.A.). The principal losses in oil yield were from cracking of oil vapor (3.0% FA for HSCB and 2.5% FA for HSFB) and from incomplete pyrolysis of kerogen (2.7% FA for HSCB and 3.2% FA for HSFB). The HSFB process had more unpyrolyzed kerogen even though it means pyrolysis temperature was higher because the four percent elutriated fines in that process were only 65% pyrolyzed. Elutriation of shale fines was lower in the HSCB retort due to the use of only a very small flow of sweep gas and the periodic venting of the pyrolysis gas along the height of the retort.

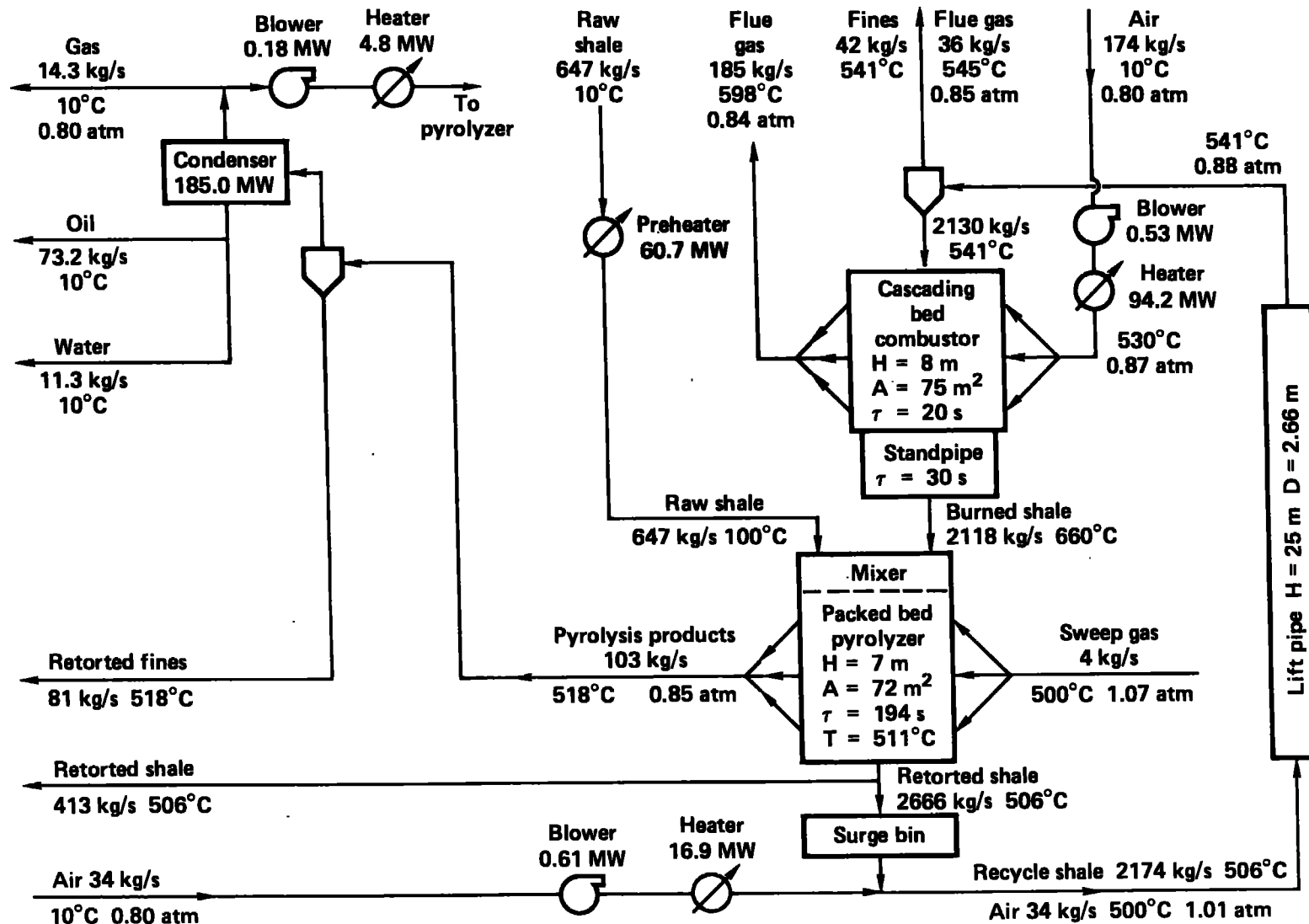
Process flowsheets are shown in Fig. 1 and 2 for HSCB and HSFB, respectively. A significant difference between the two systems is that the total reactor volume required for a 50,000 barrel/day plant was only 1387 m³ for HSCB compared with 3848 m³ for HSFB. This is primarily due to the

difference in lift pipe sizes (139 m^3 corresponding to a height of 25 m and a diameter of 2.66 m for HSCB, in contrast with 2798 m^3 corresponding to a height of 46 m and a diameter of 8.8 m for HSFB). The large lift pipe for HSFB was sized primarily to provide enough residence time for attaining the required degree of char and sulfur combustion. The small lift pipe for HSCB was sized for rapid pneumatic transport of the recycle shale to the top of the cascading-bed combustor. Even with the additional volume of 600 m^3 for the cascading-bed combustor (height of 8 m and cross-sectional area of 75 m^2) the total combustor and lift pipe volume for the HSCB system is nearly a factor of four smaller than the HSFB lift pipe combustor.

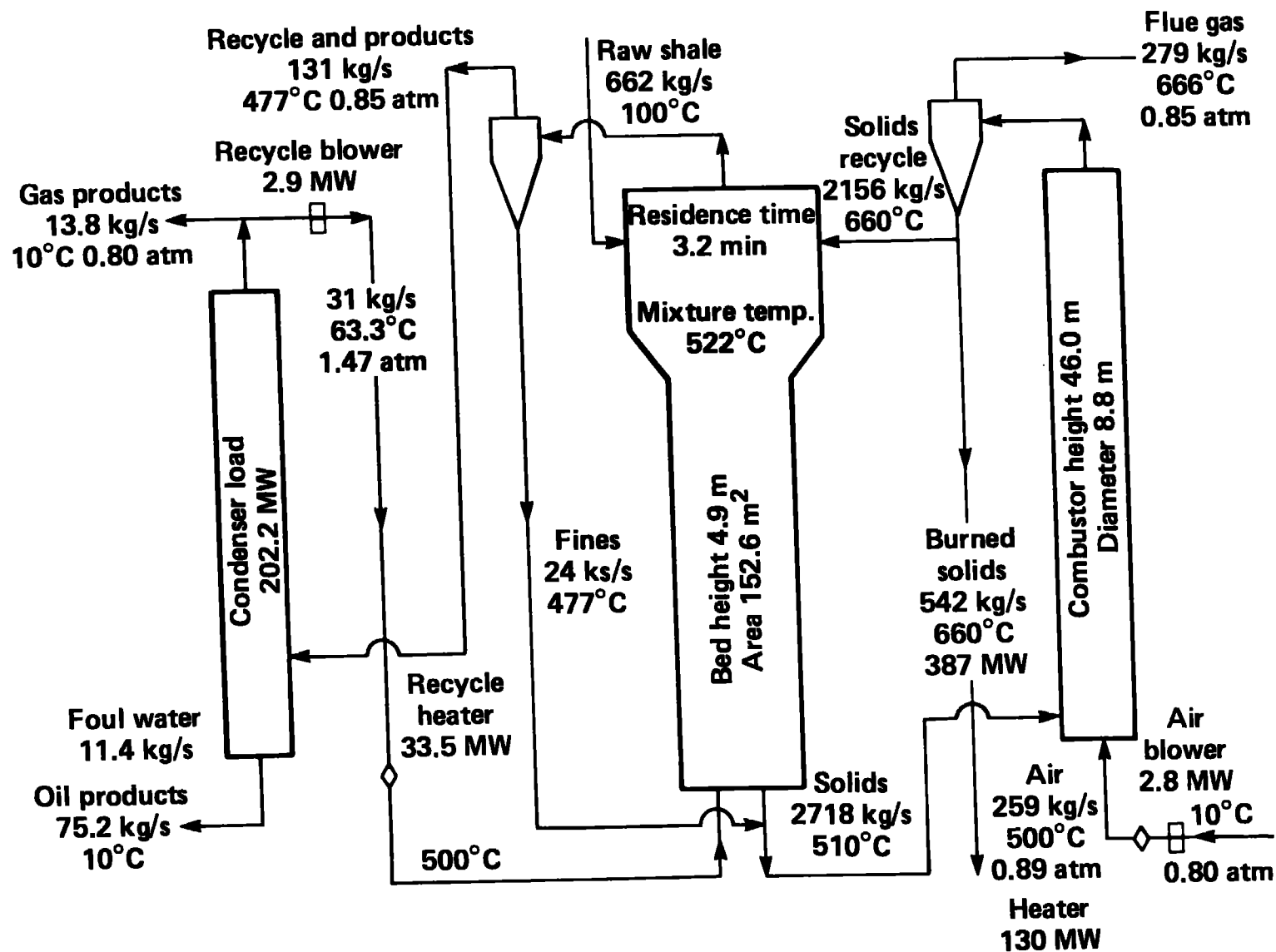
The required volume for the gravity-flow mixer/pyrolyzer in the HSCB process (648 m^3) was also smaller than that for the staged, fluidized-bed pyrolyzer in the HSFB process (1050 m^3). This is due to the smaller void fraction in the HSCB packed-bed pyrolyzer (0.40 versus 0.60 for HSFB) and the use a larger cross-sectional area for the top stage of the HSFB retort to prevent excessive elutriation of partially-pyrolyzed shale fines.

We have completed a parameter study for the HSFB system. The effects of changes in raw shale grade, recycle shale ratio, duration of oil cracking, lift-pipe operating pressure, surge bin residence time, unretorted kerogen in elutriated fines, and oxygen-enriched air have been studied. The results of these calculations help identify the relative importance of the various operating and design parameters. This will be the subject of a separate report.

50,000 barrel/day cascading bed retort system



50000 barrels/day fluidized bed retort system



PYROL Model

The general kinetics model (PYROL) for oil shale pyrolysis has been completely re-written to include additional gas and solid species and additional reactions. There are now 32 gas species (including 11 cokable oil vapor species and 11 noncokable oil vapor species), 41 condensed-phase species (including 11 cokable oil liquid species and 11 noncokable oil liquid species), and a total of 117 chemical reactions. The principal new reactions included are hydrogenation of oil (22 reactions) and hydrogenation of char (3 reactions). More accurate rate parameters for these hydrogenation reactions are still needed. The dependence on hydrogen partial pressure has also been included for kerogen pyrolysis stoichiometry. The model will next be tested by comparison with data from previous pyrolysis experiments of Singleton and Burnham. The revised and validated model should be helpful in determining the importance of retorting at elevated hydrogen pressures.

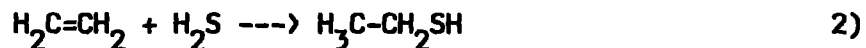
II. RETORT GASES AND THERMODYNAMIC EQUILIBRIUM

It has been widely accepted that kinetic control defines the products of an oil shale retort. This mode of behavior differentiates an oil shale retort from a coal liquefaction unit where products are produced under equilibrium conditions. One consequence of kinetic control is that a systems analysis based on reaction kinetics is of particular value for a full understanding of oil shale pyrolysis.

Certain local equilibria that might be established under retorting conditions have been investigated by a number of workers including A. Burnham, R. Crawford and P. Miller. Burnham (UCRL-84048) concluded that even when substantial cracking of the oil occurred, reaction 1) did not reach thermodynamic equilibrium at temperatures normally used for retorting.



However, reaction 2) was found to be at or near thermodynamic equilibrium ("E&TR", LLNL, Jan., 1984).



Pyroprobe work at high vacuum by Crawford and coworkers (UCRL-89361) suggests that reaction 2) is not at equilibrium under vacuum retorting conditions. The ratio of gases is about the same as found when pyrolysis is carried out at one atmosphere. This result leaves open the possibility that the near equilibrium gas ratio under atmospheric pressure conditions is coincidental.

The fluidized bed retort with gas recycle is a particularly good experimental tool for investigating equilibration of retort gases. However, efforts to identify local equilibria have generally been unsuccessful. Apparently, one or more of the following problems have frustrated these attempts:

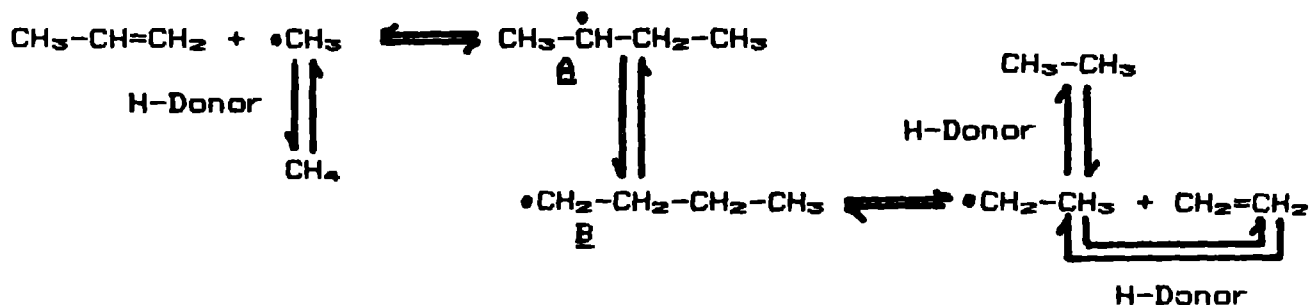
A) 5% of the isolated gas experiences no recycle (another 5% is only recycled once). Primary reaction products which reduce to trace species following equilibration can be present at an unacceptable level in the unequilibrated portion of the gas.

B) Mobile equilibria may experience additional equilibration during the cooling process.

C) Hydrogen donors, not H_2 , apparently establish the reducing potential of the system and reactions involving H_2 and/or hydrogen donors are especially difficult to study accurately.

Whether such problems are real or imagined, the ideal reaction for a study of gas phase equilibration would be one that A) had all components present at significant levels (no trace components, so K_{eq} approximately equal to one), B) had an equilibrium constant that varied little over the temperature range of interest, 0-500°C, and C) did not involve hydrogen or hydrogen donors. No such reaction can be identified for hydrocarbon gases, since restriction C) cannot be avoided. As a simplified schematic of the reaction mechanism shows (see Figure 3), the nature of hydrocarbon products depends on the hydrogen donor potential of the reaction medium.

PRINCIPAL MECHANISM OF LINEAR HYDROCARBON FORMATION



At 500°C the equilibrium constant for reaction 3) is 0.019. Reaction stoichiometry requires equal molar amounts of ethylene and ethane and equal molar amounts of propylene and methane. Under gas recycle conditions nearly equal amounts of ethane and ethylene are obtained. The most important interfering reactions, including the hydrogen donor problem, convert ethane to ethylene or ethylene to ethane. As a good approximation for calculating the equilibrium constant, ethane can be set equal to ethylene and both equal to $([C_2H_6]_{exp} + [C_2H_4]_{exp})/2$. Propylene is an excellent radical scavenger and highly susceptible to competing reactions. On the other hand, the methyl radical cannot undergo hydrogen atom elimination and cracking, so it predominantly forms methane. The left side of the equilibrium is best estimated from $([CH_4]_{exp})^2$

so,
$$K_{eq} = [(C_2H_6]_{exp} + [C_2H_4]_{exp})/2[CH_4]_{exp}]^2.$$

Table 1 gives the gas analyses and K_{eq} calculated in this way for all the gas samples taken during the large scale fluidized bed experiments with gas recycle (R-2 to R-7; on the average gas was recirculated 20 times) and with inert gas fluidization (R-1; no recycle).

Table 1: Gas Analysis Data for Calculation of the
Equilibrium Constant and Corcoran's "Beta"

SAMPLE		Gas Chromatography Results, % by Volume				K _{eq}	"beta"
		C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	CH ₄		
R-1	10:45	0.18	0.19	0.17	0.56	0.1091	0.5068
	11:31	0.20	0.20	0.18	0.60	0.1111	0.5128
	12:28	0.20	0.18	0.17	0.59	0.1037	0.5000
R-2	# 1*	1.98	1.68	1.78	5.55	0.1087	0.4993
	# 3*	2.04	1.71	1.82	5.71	0.1078	0.4980
	# 9*	2.47	2.01	2.15	6.78	0.1092	0.5017
	#11*	2.54	2.04	2.24	7.02	0.1064	0.4946
R-3	# 3	2.07	1.82	1.73	6.10	0.1017	0.4968
	# 9	2.76	2.37	2.26	8.00	0.1028	0.5000
	#13	3.09	2.57	2.48	8.87	0.1018	0.4987
	#15	3.31	2.72	2.61	9.40	0.1029	0.5021
R-4	# 4	2.19	1.78	1.77	6.40	0.0962	0.4859
	# 9	2.49	2.00	1.99	7.25	0.0959	0.4859
	#17	3.11	2.38	2.37	8.85	0.0962	0.4893
	#23	3.27	2.45	2.41	9.31	0.0944	0.4881
R-6	# 2	1.78	1.47	1.45	5.12	0.1007	0.4947
	# 9	2.28	1.79	1.80	6.58	0.0956	0.4857
	#20	2.52	1.91	1.95	7.18	0.0952	0.4852
	#30	2.73	2.03	2.06	7.65	0.0968	0.4902
	#41	2.80	2.04	2.07	7.85	0.0950	0.4879
	#47	2.87	2.07	2.13	7.85	0.0990	0.4950
R-7	# 5	2.57	2.26	2.18	7.56	0.1020	0.4959
	#11	3.46	2.83	2.77	9.86	0.1017	0.4980
	#21	3.97	3.01	3.05	11.13	0.0983	0.4922
	#31	3.75	2.67	2.77	10.57	0.0922	0.4813

In light of assumptions required to minimize the hydrogen donor problem, the agreement of experimentally determined equilibrium gas ratios with what one calculates from thermodynamic tables at 500°C (0.019) is remarkably good. The reaction evaluated is rather complex. If it reaches equilibrium, it is likely that all hydrocarbon gases in the system are at thermodynamic equilibrium,...even without recycle (see experiment R-1 in Table 1).

An alternative means of evaluating the gas analysis data from the fluidized bed retort leads to the same conclusions (i.e., complete, or at

least extensive, gas phase equilibration). The alternative method of analysis is based on studies of butane pyrolysis carried out in the laboratory of W. H. Corcoran [Blakemore, Baker, and Corcoran, Ind. Eng. Chem., Fundam., 12, 147 (1973)]. The secondary butyl radical (A of Figure 4) yielded methane plus propylene and the primary butyl radical (B of Figure 4) yielded ethane plus ethylene. In the absence of other reactions that make or destroyed these product gases, the ratio of ethane plus ethylene to methane plus propylene was equal to the relative thermodynamic stability of the two butyl radicals. This ratio was defined as "beta":

$$\beta = \frac{([C_2H_6] + [C_2H_4])}{([CH_4] + [C_3H_6])}$$

The ratio is insensitive to temperature variation and is equal to 0.5 at thermodynamic equilibrium. Thus restrictions A), B), and C) are all avoided.

The kinetics of formation of these high energy intermediates reflect thermodynamic stabilities since the transition states are very product-like in character. The butane pyrolysis experiments of Blakemore, Baker and Corcoran were apparently done under conditions of kinetic control. However, butane is not present in kerogen or bitumen, so the mechanism of gas formation from oil shale (Figure 4) must be entered via the free radical intermediates that result from cracking (mainly via the primary butyl radical, B). The finding that Corcoran's "beta" is at the thermodynamic level requires equilibration of butyl radicals under oil shale pyrolysis conditions.

The values of Corcoran's "beta" have been included in Table 1. Table 2 give the average "beta" value, along with standard deviation and high and low values for all analyses (25 total) taken during large-scale fluidized bed retorting experiments.

Table 2: Corcoran's "Beta": $([C_2H_6] + [C_2H_4])/([CH_4] + [C_3H_6])$

AVERAGE 0.4946

ST. DEVIATION 0.0074

HIGH 0.5128

LOW 0.4813

The standard deviation, $\pm 1.5\%$ of the average value, is as good as the gas analysis repeatability. The high and low values were from samples obtained under unusual experimental conditions: no gas recycle in the case of the high value, interrupted solid flow in the case of the low value. The average value is identical to that determined in the previously referenced butane pyrolysis investigation.

It is rare to obtain a gas ratio, "beta", that suggests butyl radical equilibration under pyrolysis conditions. Autoxidation results in a value higher than that expected based on relative thermodynamic stabilities of the radicals; reactions that destroy components of the gas result in a lower than expected ratio. Reports regarding polyethylene pyrolysis and hexadecane cracking have lower than expected values of "beta". Fischer assays of oil

shale have low values (perhaps, due to unequilibrated methane from char pyrolysis). Results from the gravity bed retort are mixed, but they tend to be high, suggesting oxidation.

Other evidence is available to support radical equilibration in the solid-recycle retort experiments. The high level of deuterium incorporation into the oil when D_2O was used as sweep gas is one example. The relatively low gas yield from the fluidized bed retort is another (and the decreased gas yield when gas was recycled).

However, direct gas phase isomerization of B to A (butyl radical equilibration) as implied by Figure 4 is unlikely. Orbital symmetry considerations do not favor a direct 1,2-shift of a hydrogen atom. A catalyst (perhaps the spent shale) or an intermediate (perhaps butane) is needed. Experiments are underway to understand the details of this equilibrium and others. In an equilibrating system, it may be possible to retort oil shale under conditions where the cracking reaction is reversed and free radical addition reactions that convert hydrocarbon gases to oil predominate.

III. HYDROGEN DONATION IN THE PYRITE TO H_2S REACTION

Previous work at LLNL has shown that H_2S is formed by both organic and inorganic sources of sulfur in the raw shale. Because pyrite (FeS_2) is the dominant source of sulfur in Colorado oil shale, we have concentrated on understanding the conversion of pyrite to H_2S . In particular, we are interested in specifying the source of hydrogen donors for the generic

reaction of the type:



We have recently conducted qualitative experiments which indicate that water may act as a hydrogen donor in the reaction written above. Experiments were conducted using a fluidized bed reactor, containing pyrite, heated to retort temperatures (520°C). When small quantities of water were added to the fluidizing gas, H₂S and SO₂ were detected in a molar ratio of 1,6:1 at the fluidizing gas, H₂S and SO₂ were detected in a molar ratio of 1,6:1 at the exit of the fluidized bed reactor. We believe the major reaction taking place is:



Analysis of the exit gas by mass spectrometry reveals that molecular hydrogen is not produced in the reactor. Thus, it would appear that the pyrrhotite (FeS) produced during reactions of the type shown in Equation 5, is stable with respect to further decomposition by water. Further data including the kinetics of this reaction will be reported in the future.

IV. QUANTITATIVE ASPECTS OF SULFUR GASES FROM OIL SHALE

The triple quadrupole mass spectrometer (TQMS) was used to analyze the

sulfur-containing gases released when oil shale was heated in a pyroprobe. This device allows a few milligrams of material to be heated in the source of the TQMS to temperatures up to 100°C and at rates ranging from a few degrees per minute to thousands of degrees per second. Since the material is heated in the high vacuum of the TQMS, very few products of secondary reactions are formed.

We analyzed the data from three different experiments to see if a somewhat quantitative comparison could be made between runs. We chose methylthiophene as a species to use in normalizing data between separate pyroprobe runs made on a particular shale treated in different ways. This compound was chosen as it is probably the result of the primary decomposition of organic molecules containing a thiophenic group. In addition, it is very thermally stable and is almost totally unaffected by the presence of pyrite in the shale. This last is illustrated in Figure 5. The upper trace shows the release of methylthiophene vs temperature for a normal oil shale. The lower trace shows the same data but the shale has been spiked with 2% by weight pyrite (FeS_2). The pyrite has been shown to cause a large increase in most other sulfur containing gases at temperatures between 450 and 550°C, but no significant increase is seen for methylthiophene. Thus, methylthiophene can be assumed to be from organic sources only.

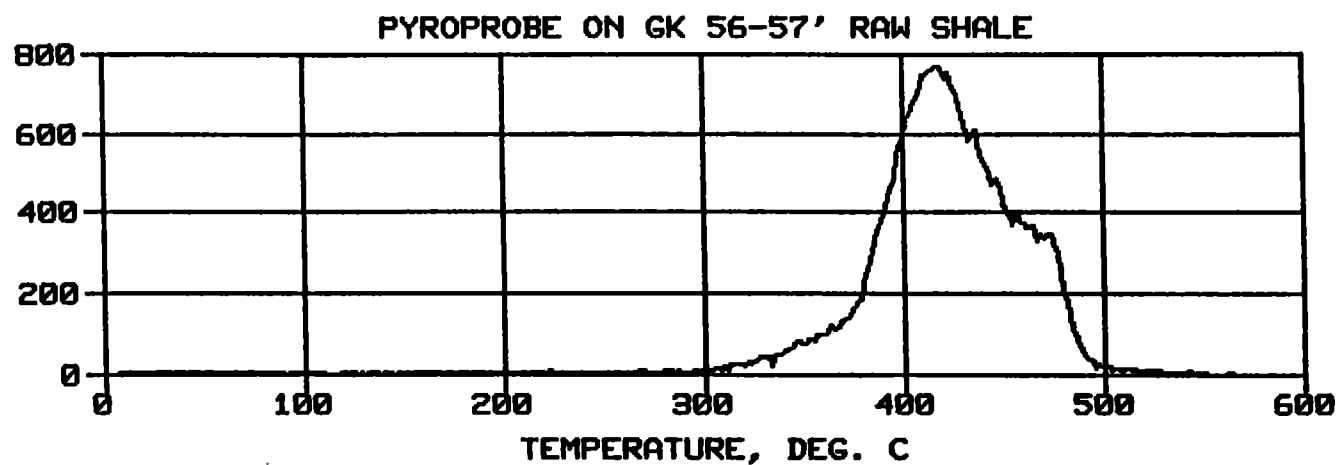
The experiments were performed on two sets of shales. The first set was a shale fairly high in sulfur, Anvil Points 24 gal/ton. Pyroprobe runs were made on the raw shale and a sample of the shale that had been treated with HCl and HNO_3 to remove the pyrite. Figure 6 shows the results for H_2S from

these two runs. It can be seen that almost no H_2S is released from the acid treated shale at the 450 to 550°C temperature range, indicating that this is in fact the temperature range where pyrite forms H_2S . In addition, since the data from these two runs has been normalized using the methylthiophene released from each, the amount of H_2S released at the lower temperature can be directly compared. It can be seen that the amounts are very similar, suggesting that H_2S released in this temperature range is not affected by pyrite content but is probably from organic sources. The almost identical result can be seen for COS in Figure 7.

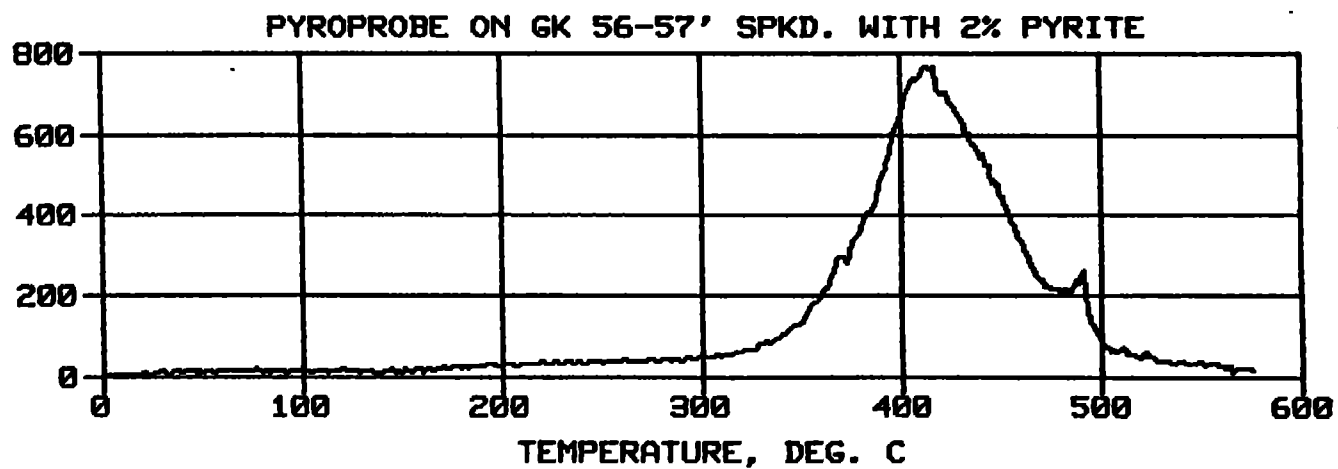
The second set of runs used a shale low in sulfur, Geokinetics 56-57'. Both raw shale and shale with 2% added pyrite were run. Figure 8 shows the results of these runs. A large additional release of H_2S is seen at the 450 to 550°C temperature range for the spiked sample, but again no difference is seen between the normalized data at the lower temperature. This verifies the fact that the pyrite does not affect the release of H_2S from the organic sources under the conditions found in the pyroprobe. thus, the pyroprobe can be used to rapidly determine a semi-quantitative differentiation between organic and pyritic sources of sulfur in oil shales. This is shown in Table 3 where the pyroprobe data is compared to a wet chemical speciation for three different shales. The organic sulfur by wet chemistry is the amount of sulfur measured after the shale is treated with HCl and HNO_3 .

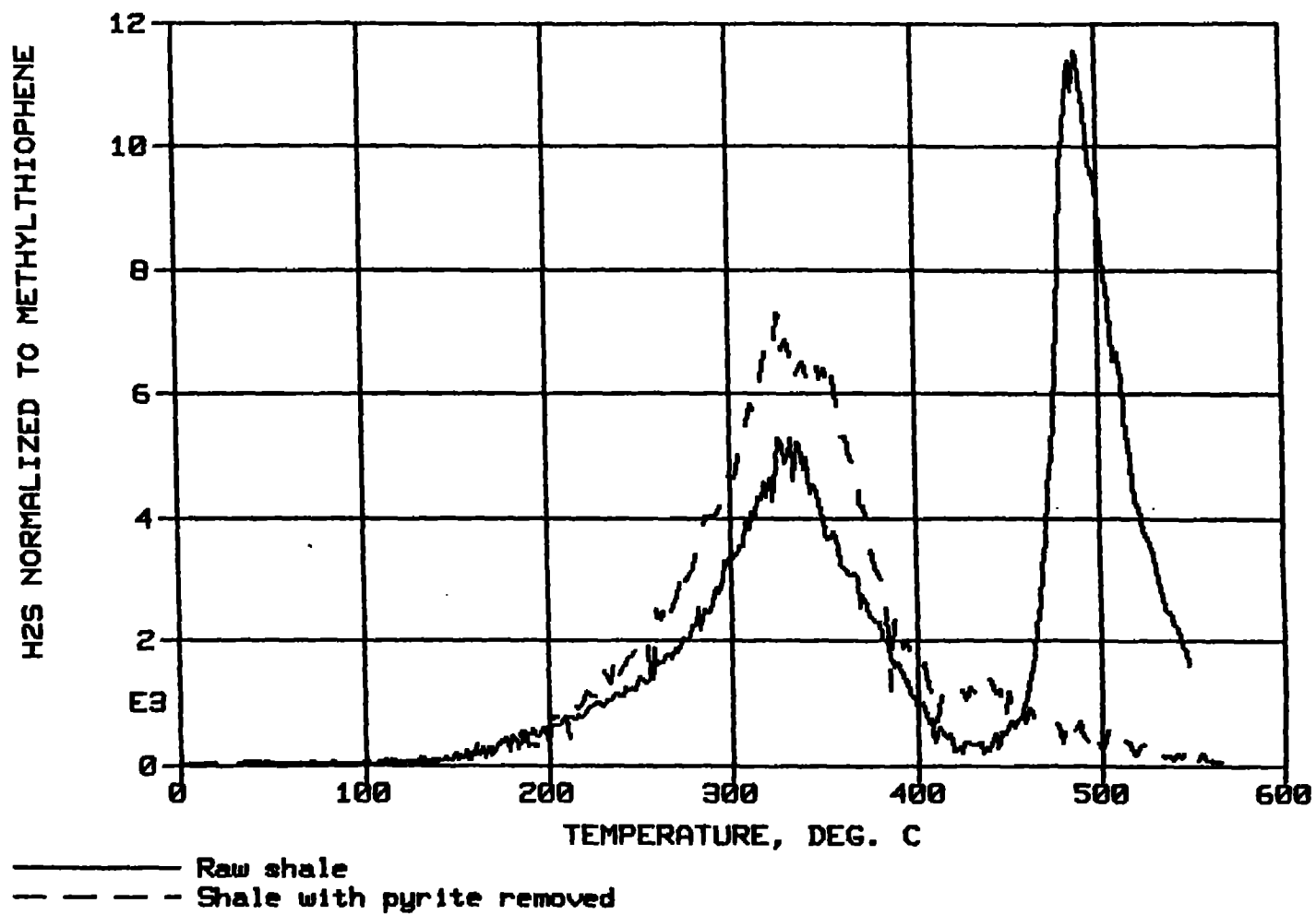
A different set of experiments was used to evaluate the quantitative ability of Fe_2O_3 to remove sulfur-containing compounds released under Fischer-assay like conditions. Pure Fe_2O_3 was added to a shale which had

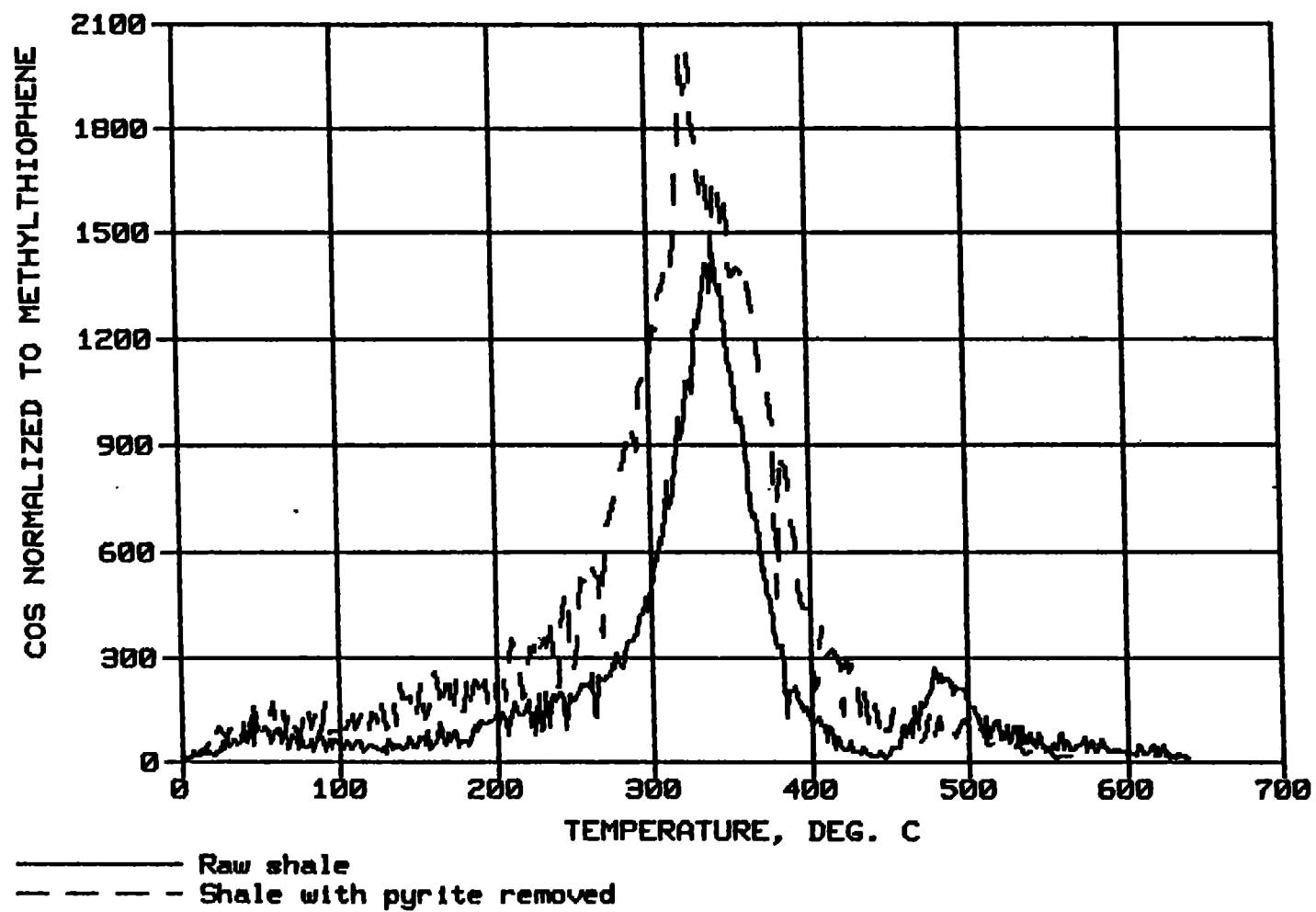
METHYLTHIOPHENE



METHYLTHIOPHENE





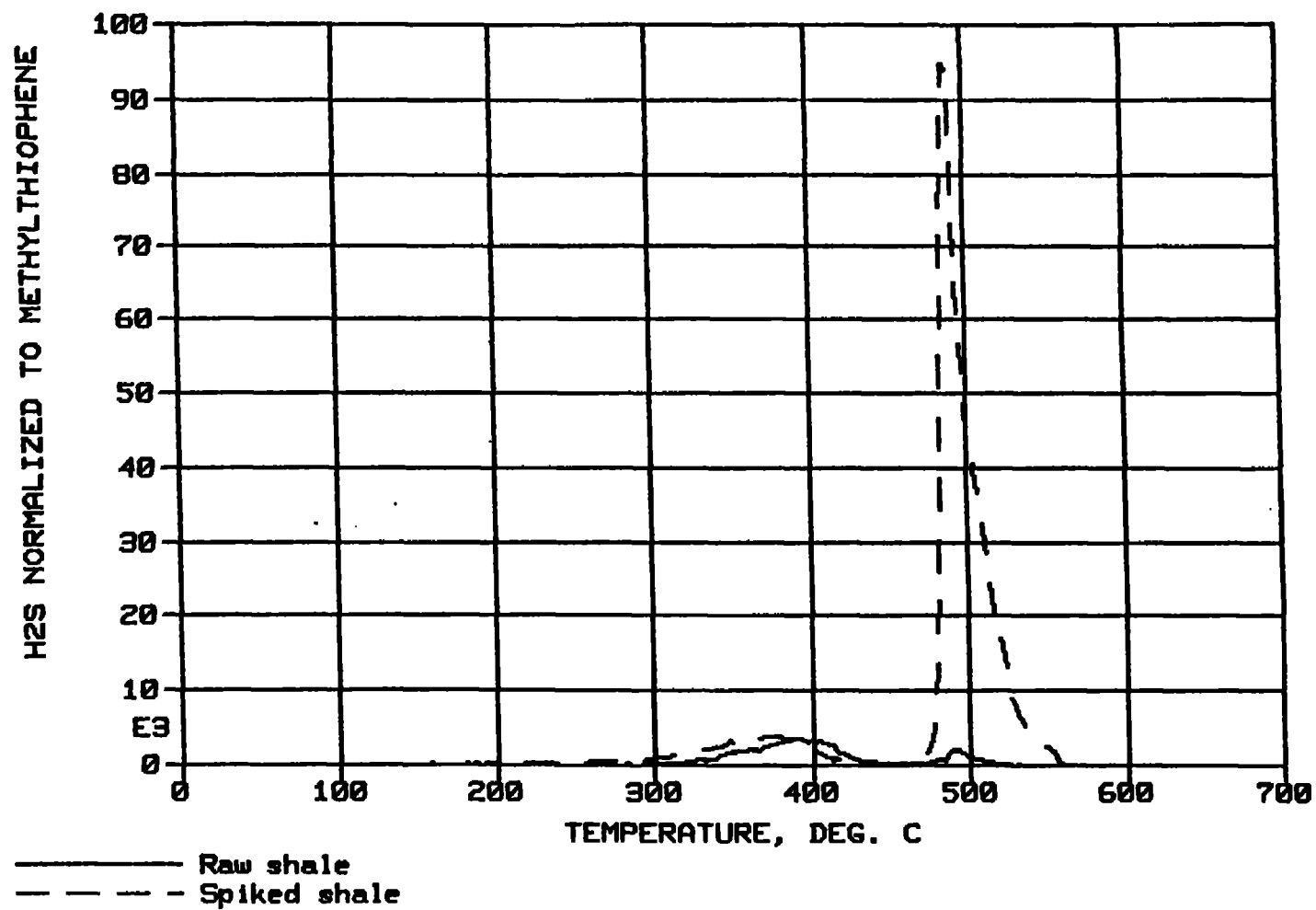


been treated with HCl to remove the carbonates. Shale samples spiked with 2, 3, and 5% Fe_2O_3 were heated at 11°C per minute to 500°C in the bulb-type apparatus connected to the TQMS. The amounts of the sulfur gases released were determined. We found that the Fe_2O_3 reacted stoichiometrically with the H_2S (two moles of H_2S for one mole of Fe_2O_3). The data for these experiments is shown in Table 4. The COS and CS₂ levels decreased linearly with Fe_2O_3 content also as seen in Figure 9.

Measurements of the scrubbing rates of combusted shale suggest that the major contributor to H_2S scrubbing is the 2 to 3% Fe_2O_3 contained in the combusted shale. To verify this, samples containing 1:1, 1:2, and 1:4 mixtures of high sulfur shale and combusted shale were run in the bulb-type apparatus. A linear decrease in H_2S , COS and CS₂ was noted as in the runs with pure Fe_2O_3 . If Fe_2O_3 is assumed to be the major scrubbing agent, a content of 2.65% Fe_2O_3 would explain the measured scrubbing. An analysis for Fe in the combusted shale shows a content very close to this amount.

Table 3 Comparison between H_2S Produced at Medium Temperatures (250-350°C) by Pyroprobe and % Organic Sulfur Determined by Wet Chemical Speciation

	% total H_2S produced at 250°C - 350°C	% organic S (wet chemistry)
Tract C-a, 18 gal/ton	21.1	14
Anvil Points, 24 gal/ton	31.5	31
Geokinetics, 56-57 ft	82.0	80



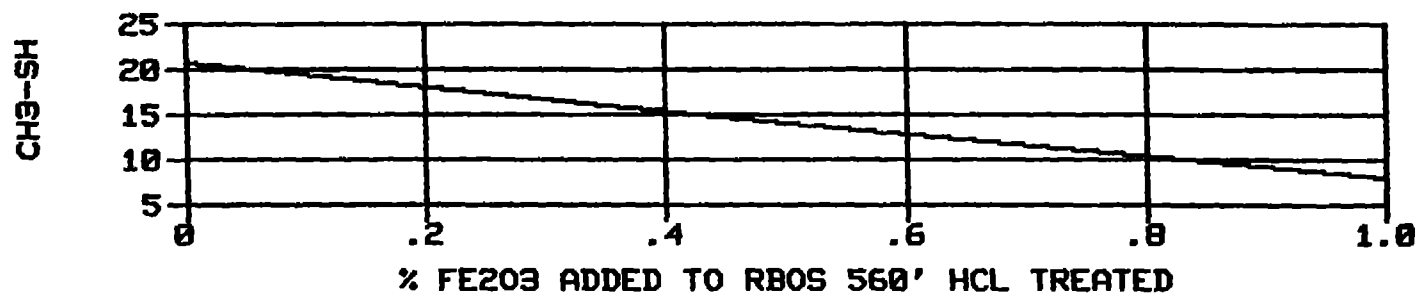
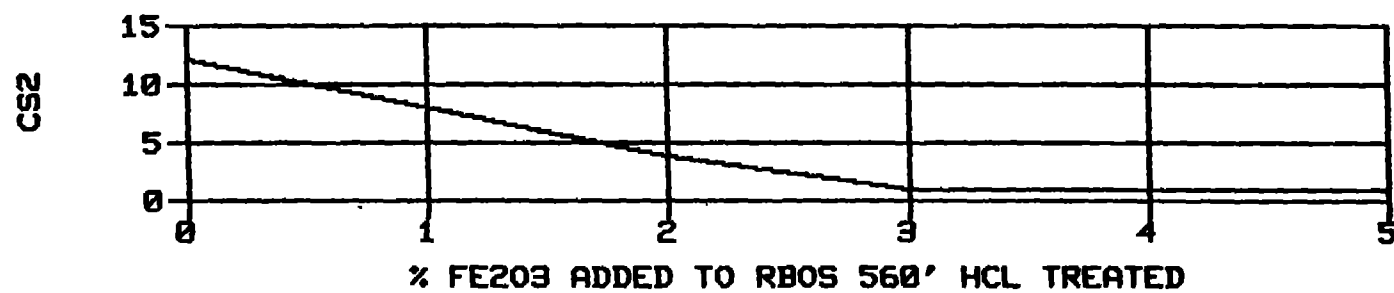
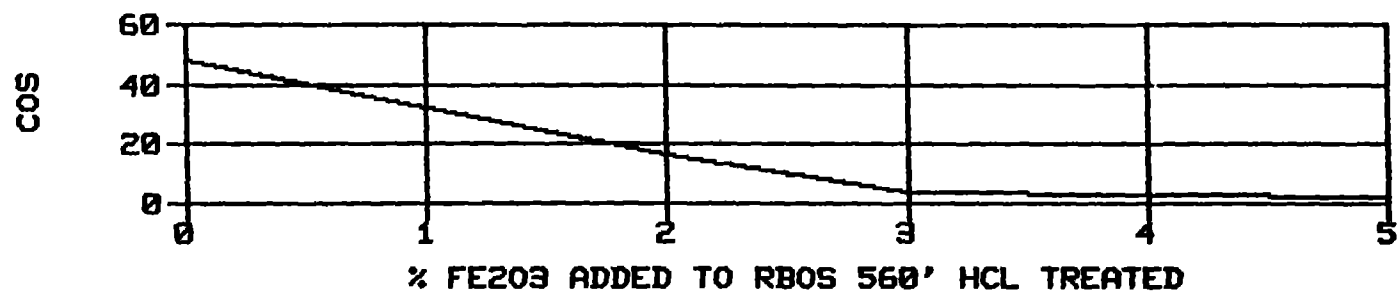
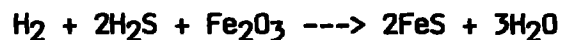


Table 3 Addition of Fe_2O_3 to Shale Shows Quantitative Removal
of H_2S using Bulb-type Reactor

Assume reaction:



The shale used was Tract C-a 5601 treated with HCl to remove carbonates

Fe_2O_3 added %	$\text{Fe}_2\text{O}_3 \times 2$ millimoles	H_2S left millimoles	H_2S used millimoles	completion %
0	0	.379	0	-
2	.250	.114	.265	106
3	.376	.011	.368	98
5	.626	.001	.378	excess Fe_2O_3